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Slow dynamics of shape recovery of disordered nematic elastomers

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A loosely cross-linked liquid crystal elastomer (LCE) having a disordered director alignment (polydomain texture) slowly recovers to their original shape from the deformed state in the order of 10^3 s after the imposed field is removed. The mesogen alignment at the cross-linking stage greatly affects the shape recovery dynamics of polydomain LCEs, whereas it has no appreciable influence on the equilibrium characteristics such as the nematic-isotropic transition temperature, degree of swelling, and field-induced strain. The shape recovery of a LCE formed in the polydomain nematic state is considerably faster than that originally prepared in the isotropic state because of the memory effect of the initial director distribution at the cross-linking stage. The relaxation time rapidly increases as the temperature approaches the transition temperatures; this is independent of the initial mesogen alignment during cross linking.

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I. INTRODUCTION

Liquid crystal elastomers (LCEs) having mesogenic groups in elastomeric polymer networks are a hybrid material of liquid crystals and elastomers. LCEs are roughly classified into two types—monodomain and polydomain LCEs—depending on the presence or absence of a globally aligned director [1]. When no special care is taken to achieve a global director orientation at the cross linking of mesogens, the resultant LCE exhibits a disordered polydomain texture without a global director but with a local nematic order in the order of microns. The cross links and defects in a network structure act as the main source of random disorder [2–4]. Each local nematic domain contains many cross-link sites because the average distance between cross links is of the order of several nanometers in typical polymer networks. Nematics with quenched disorder have received considerable attention owing to a variety of interesting properties [5–7]. The behavior of nematic liquid crystals embedded in disordering host structures such as random porous media was widely investigated. The random disorder in these systems arises from the anchoring on the surface of the random porous media. The length scale of the source of the quenched disorder is similar to or larger than the domain size of the resultant texture. Polydomain LCEs and such disordered LC systems differ in terms of the source and length scale of the random disorder [3]. Polydomain LCEs are similar to spin glasses and random magnets in terms of the spatial correlations of alignments [3] because they consist of random local domains and have no overall alignment.

A familiar phenomenon specific to polydomain LCEs is the polydomain-to-monodomain (P-M) transition driven by stretching [8–11]. Uniaxial stretching transforms the disordered director texture into a uniformly aligned state, and the resultant stress is considerably low and remains almost constant during the transition. Terentjev *et al.* observed a slow stress relaxation under a constant strain during the P-M transition [12,13]. These behaviors in the P-M transition were

attributed to the soft elastic response of rotating nematic domains [3] or the spatial heterogeneity caused by many small domains [14].

Our previous studies [15–17] revealed an electrically driven deformation behavior of the LCEs swollen by low-molecular-mass LCs. A striking difference between monodomain and polydomain LCEs is the time required to recover to the original shape from a deformed state after the removal of the imposed field. The shape recovery of a monodomain LCE undergoes rapidly within 1 sec whereas a polydomain LCE shows a markedly slow shape recovery in the order of 10^3 s [16]. This implies that the slow strain recovery of the polydomain LCEs primarily stems from the polydomain nature rather than the viscoelastic relaxation due to the chain-entanglement effect. Polydomain LCEs are obtainable via two different routes. The first is by cross linking the mesogenic monomers in the low-temperature polydomain nematic state. The second is by cross linking the mesogens in the high-temperature isotropic state and cooling the resultant networks into the low-temperature nematic state. We designate an LCE prepared via the former and latter routes as NLCE and ILCE, respectively. The initial director distribution at the cross-linking stage is expected to affect the physical properties of the resultant polydomain LCE. A simulation study by Uchida [4] showed that NLCEs have a stronger disorder correlation than ILCEs, and their P-M transition behaviors are significantly different. The physical properties of these two types of polydomain LCEs, however, have not been fully studied through experiments. The experimental work of Küpfer *et al.* [9] compared the phase behavior and tensile properties of the LCEs prepared in the nematic and isotropic states but mostly under an extensional load. Their main focus was on the effect of extensional loading at cross linking on the properties of the resultant LCEs, and the data for the pure polydomain LCEs formed without extensional loads are considerably limited. Another experimental work [11] includes the data for the P-M transition of ILCEs and NLCEs, but unfortunately, the cross-linking condition for each stress-strain data is not explicitly described in the literature. The behavior of polydomain LCEs near the nematic-isotropic transition temperature is also an interesting issue of investigation. Regarding the static features,

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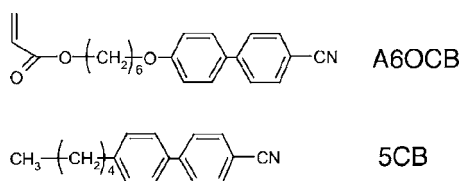


FIG. 1. Molecular structures of A6OCB and 5CB.

Clarke *et al.* [18] showed that the domain size of polydomain LCEs rapidly evolves near the transition temperature with a decrease in the local nematic order. In contrast, the dynamic features of polydomain LCEs near the transition temperature have not yet been investigated. In the present study, we compare the slow dynamics of the shape recovery of ILCEs and NLCEs with the same concentration of the cross-links. We also examine the temperature dependence of the characteristic time for the shape recovery of these two networks in the vicinity of their transition temperatures.

II. EXPERIMENTAL SECTION

A. Sample preparation

A side-chain-type LCE was prepared by photo-cross-linking an acrylate mesogenic monomer (A6OCB in Fig. 1) and 1,6-hexanediol diacrylate (cross linker) using Irgacure 784 (photoinitiator). A miscible nonreactive low-molecular-mass LC, 4-*n*-hexyloxy-4'-cyanobiphenyl (6OCB), and A6OCB were mixed in a weight ratio of 4:5 to broaden the temperature range of the nematic state. The cross-linker concentration was 1 or 7 mol. % in the feed. Photo-cross-linking was performed in a glass cell (without surface treatment for mesogen alignment) with a gap of 20 μm . Cross linking was performed at two temperatures—90 °C in the isotropic state and 45 °C in the polydomain nematic state of the nematic mixture (with a N-I transition temperature of 50 °C). The resultant networks were designated as ILCEX and NLCEX, respectively, where X denotes the cross-linker concentration. The film samples were carefully separated from the cell, and the unreacted materials and nonreactive nematogen (6OCB) were washed out from the networks by swelling in dichloromethane. After deswelling in methanol and drying in air, the networks were allowed to swell in a low-molecular-mass LC, 4-*n*-pentyl-4'-cyanobiphenyl (5CB in Fig. 1).

B. Measurement

Rectangular film samples with a length and width of ~ 2 mm each were placed in a transparent glass cell with ITO electrodes as shown in Fig. 2. The cell gap (40 μm) was larger than the film thickness so that the samples were not mechanically constrained by the electrodes. The cell was filled with the swellant, 5CB. The temperature was controlled by the Mettler Hot Stage FP-82. After the swelling was equilibrated at each temperature, a sinusoidal electric field with a frequency of 1 kHz and a voltage amplitude of 600 V was applied in the thickness direction for 60 s to induce an electrically driven distortion. After the removal of the

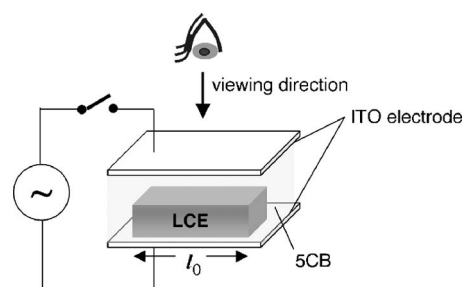


FIG. 2. Shape recovery experiment.

field, the film length l (in a direction normal to the field axis) was measured as a function of time (t) by polarized microscopy. The corresponding strain $\gamma(t)$ is defined as

$$\gamma(t) = [l(t) - l^0]/l^0, \quad (1)$$

where $l(t)$ and l^0 are the lengths at the time of interest and in the undeformed state, respectively. As the dielectrically positive polydomain LCEs are uniaxially stretched in the field direction [16], γ becomes negative upon the field application owing to lateral shrinking. After removing the imposed field, γ approaches zero as the sample recovers to the original shape. The distortions in two principal directions normal to the thickness (field) direction did not exhibit anisotropy. The imposed fields did not cause the P-M transition, and the samples exhibited a polydomain texture throughout the measurement. The degree of equilibrium swelling (Q : the volume ratio of the fully swollen to the dry network) was evaluated by $Q = (l_s/l_d)^3$ where l_d and l_s are the lengths in the dry and swollen states, respectively, because the swelling shows no anisotropy owing to the polydomain texture. The nematic-isotropic transition temperatures of each sample in the dry and fully swollen states were determined by polarized microscopy.

III. RESULTS AND DISCUSSION

A. Equilibrium characteristics

Table I summarizes Q and the N-I transition temperatures of ILCEs and NLCEs in the dry and fully swollen states. In the fully swollen state, the nematic network and the swellant formed a single nematic phase. The temperature T_{NI}^G corresponds to the transition temperature of a miscible nematic

TABLE I. Characteristics of the LCE samples.

LCE	Crosslinker concentration ^a (mol. %)	Q^b	T_{NI}^N (°C)	T_{NI}^G (°C)
ILCE1	1	14.8	134	48.1
NLCE1	1	14.6	135	48.8
ILCE7	7	3.94	123	49.7
NLCE7	7	4.06	122	50.3

^aMolar fraction of the crosslinker in all the reactants.

^bMeasured at 25 °C.

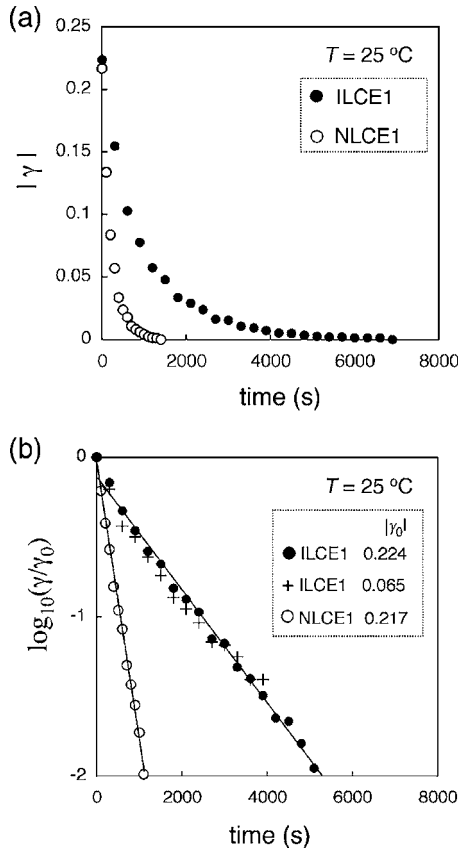


FIG. 3. (a) Time dependence of γ during the shape recovery of ILCE1 and NLCE1 at 25°C . The data at $t=0$ correspond to the strain induced by the applied field (γ_0). (b) Semilog plots of γ/γ_0 vs time. The cross symbols represent the shape recovery of ILCE1 from a smaller γ_0 induced by a lower field. The inverse of the slope yields the longest relaxation time $\tau=1.4\times 10^3$ for ILCE1 and 2.6×10^2 s for NLCE1.

mixture of the network and the solvent with a network volume fraction of Q^{-1} at T_{NI}^G . As is evident in Table I, if the cross-linker concentrations are identical, the difference in the nematogen alignment at the cross-linking stage yields no appreciable difference in these equilibrium properties. Similar results for Q and T_{NI}^N were obtained in Ref. [9] for the samples prepared without extensional load at cross linking. Almost the same values of Q indicate that NLCEX and ILCEX have the similar amount of cross-linker truly incorporated into the network, because Q primarily depends on it [19]. No appreciable difference in the N-I transition temperatures suggest that NLCEX and ILCEX are almost similar in the local nematic order.

An increase in the cross-linker concentration results in a slight increase in T_{NI}^G as well as a decrease in Q and T_{NI}^N . The results in our previous study [19] show the same tendency; this is discussed in detail in Ref. [19].

B. Shape recovery dynamics

Figure 3(a) illustrates $\gamma(t)$ of ILCE1 and NLCE1 at 25°C . The data at $t=0$ corresponds to the strain induced by the applied field (γ_0); $\gamma_0=-0.224$ and -0.217 in ILCE1 and

NLCE1, respectively. A difference in the mesogen orientation at the cross-linking stage causes no appreciable difference in γ_0 ; this is similar to the equilibrium characteristics mentioned in the previous section. However, the dynamics of the shape recovery of these two networks is significantly different. The shape recovery of ILCE1 is considerably slower than that of NLCE1— γ reaches zero at $t\approx 6.0\times 10^3$ and 1.7×10^3 s in ILCE1 and NLCE1, respectively. Figure 3(b) displays the semilogarithmic plot of γ/γ_0 versus time. Most of the data points trace a straight line. This indicates that the shape recovery process obeys an exponential-type relaxation as follows:

$$\frac{\gamma(t)}{\gamma_0} = \sum_{i=1} A_i \exp\left(-\frac{t}{\tau_i}\right), \quad (2)$$

where A_i and τ_i are the strength and characteristic time of the i th mode, respectively. An attempt to fit another type of relaxation function such as a stretched exponential function and power law was made, but the quantitative fit to the data was unsuccessful. The slow stress relaxation of a polydomain LCE in the dry state was reported to obey a power law or inverse-logarithm function depending on the time regime of interest [12]. The reason for the difference in the relaxation function for the shape recovery and stress relaxation is unclear; however, it should be noted that in the swollen LCE examined here, the contribution of chain-entanglement relaxation (observed in the stress relaxation of conventional rubber [20]) is highly diluted due to the low network concentrations. The shape recovery data of the corresponding LCE in the dry state is needed for further discussion; unfortunately, the electrically induced distortion in the dry LCE is too small to quantify owing to the high elastic modulus, which precludes the shape recovery experiment.

As seen in Fig. 3(b), the kinetics is almost approximated by a single-exponential-type relaxation, although a finite contribution of the fast modes of $i\geq 2$ is recognizable in ILCE1 by a deviation from the linear correlation at short times. The longest characteristic time ($\tau_1\equiv\tau$) is evaluated from the inverse of the slope of the straight line. The value of $\tau(=1.4\times 10^3$ s) of ILCE1 is approximately five times larger than that ($\tau=2.6\times 10^2$ s) of NLCE1. The shape recovery from a smaller initial strain of $\gamma_0=-0.065$ induced by a lower field exhibits almost the same dynamics, as shown in Fig. 3(b). This shows that the shape recovery dynamics is independent of γ_0 within the examined range.

The LCE7 networks with a higher cross-linker concentration show the same trend as LCE1. As shown in Fig. 4, $\tau(=6.6\times 10^1$ s) of ILCE7 is approximately nine times larger than that ($\tau=7.3$ s) of NLCE7, whereas no appreciable difference in γ_0 is observed between these two networks. Figure 4 also includes the data of a NLCE (designated as NLCE7L) with the identical cross-linker concentration but cross linked at a temperature of 33°C that is 12°C lower than the cross-linking temperature of NLCE7 (45°C). Local nematic order of the polydomain mesogens (before cross linking) is expected to increase with decreasing T , but the cross-linking temperature in the polydomain nematic state does not signifi-

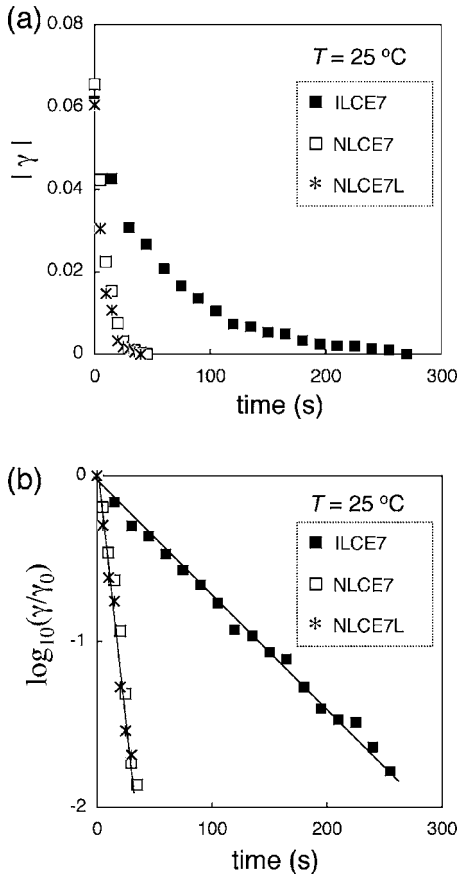


FIG. 4. Time dependence of γ during the shape recovery of ILCE7 and NLCE7 at 25 °C. The data at $t=0$ correspond to the strain induced by the applied field (γ_0). The data of N-LCE7L crosslinked at a lower temperature (33 °C) as compared to NLCE7 (45 °C) are also displayed. (b) Semilog plots of γ/γ_0 vs time. The inverse of the slope yields the longest relaxation time $\tau=6.6 \times 10^1$ s for ILCE7 and 7.3 s for NLCE7.

cantly influence the shape recovery of NLCEs within the examined range.

A swollen monodomain LCE ($Q=4.10$) of a cross-linker concentration of 7 mol. % prepared under the same condition but using a surface-treated cell shows a perfect shape recovery within 1 s. This is considerably faster than the time (~ 35 s) for NLCE7 with the same cross-linker concentration. This clearly indicates that the slow shape recovery of polydomain LCEs mainly originates from the polydomain nature.

An increase in the cross-linker concentration reduces τ as well as γ_0 . These primarily stem from an increase in the elastic modulus (G_s) governing the restoring force of rubber elasticity. As the first approximation, τ is proportional to the ratio η/G where η is a viscous coefficient governing the resistant force and G is an elastic constant representing the restoring force. According to the classical theory of rubber elasticity [21], the modulus of swollen networks (G_s) is given by $G_s=G_d Q^{-1/3}$ where G_d is the dry modulus. When we simply assume that G_d is proportional to the cross-linking density, the G_s ratios of LCE1 and LCE7 are evaluated to be ~ 11 for both ILCEs and NLCEs. The ratio of τ of ILCE1

and ILCE7 (or NLCE1 and NLCE7) is ~ 21 (or ~ 36), both of which are larger than but in the same order as the ratio of G_s . Although this estimation of G_s is crude, similar ratios regarding G_s and τ suggest that a difference in τ of the networks with different cross-linking densities at the same temperature is dominated by the difference in network moduli rather than η and the Frank constants affecting G . The smaller γ_0 of LCE7 as compared to LCE1 mainly originates from the high modulus. A further detailed estimation of the cross-linking density effect on γ_0 from the present data is not straightforward because the effective field strength acting on the film specimen in the unconstrained geometry complicatedly depends on the solvent content as well as the film thickness, both of which vary with the cross-linking density. Huh *et al.* [22] also examined the shape recovery process for a swollen polydomain LCE, but the observed dynamics was not so slow as to attract their attention. This is probably because of its considerably high cross-linker concentration, although they did not describe the cross-linker concentration of their sample.

The considerably faster shape recovery of NLCEs as compared to ILCEs indicates that the cross linking in the polydomain nematic state acts to memorize the initial director distribution before cross linking into the resultant networks. This memory effect yields a stronger director correlation in NLCEs as compared to ILCEs originally formed in the isotropic state. This difference in the strength of the director correlation is clearly observed in the shape recovery dynamics, whereas it has no appreciable influence on the equilibrium and static properties such as T_{NI}^N , T_{NI}^G , Q , and γ_0 (i.e., no noticeable effect on the local nematic order). The simulation study by Uchida [4] showed that the strain-induced P-M transition in ILCEs yields almost zero stress whereas that in NLCEs generates a finite stress. Uchida concluded that the memory of the initial director distribution in NLCEs acts as a strong correlated quenched disorder, and this creates a *non-soft* mechanical response in contrast to the *soft* mechanical response of ILCEs. Terentjev *et al.* [12,13] observed a remarkably slow stress relaxation in ILCEs and attributed it to the reorientation of each domain via a soft-deformation pathway. The slow shape recovery in the present study will have the same origin as the P-M transition with a small plateau stress and the slow stress relaxation, although we cannot observe the mechanically induced P-M transition for the swollen LCEs owing to their poor extensibility. The slow shape recovery of the polydomain LCEs reflects the slow recovery to the initial disordered polydomain texture, and the strong director correlation generated at the crosslinking stage acts to accelerate the recovery.

C. Temperature dependence of characteristic time

Figures 5 and 6 show $\gamma(t)$ of ILCE1 and NLCE1 at various temperatures on cooling toward 25 °C, respectively. The strains are reduced by γ_0 at each temperature listed in Table II. For both the systems, the shape recovery becomes slower near T_{NI}^G when $T \rightarrow T_{NI}^G$. Figures 5(b) and 6(b) show that the shape recovery kinetics in the whole T range examined is described by the exponential relaxation.

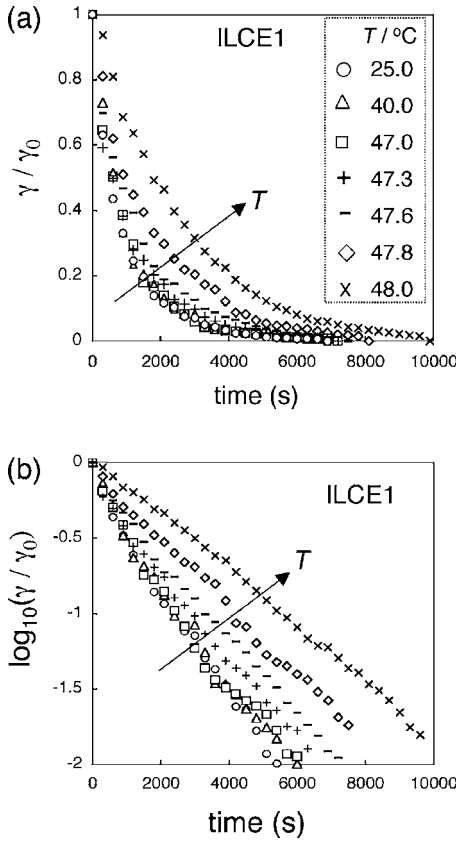


FIG. 5. (a) Time dependence of γ during the shape recovery of ILCE1 at various temperatures. The strain $\gamma(t)$ is reduced by the initial strain at each temperature. (b) Semilog plots of γ/γ_0 vs time at various temperatures. Symbols are the same as (a)

Figure 7 illustrates the T dependence of τ of ILCE1 and NLCE1. For both the networks, τ steeply increases with T in the region near T_{NI}^G [$(T_{NI}^G - T) < 1$ °C]. In this T region, the degree of swelling (Q) is almost constant or slightly decreases with increasing T as shown in Table II. This means that the network modulus ($G_s \approx G_d Q^{-1/3}$) [21] is almost unchanged or slightly increases when $T \rightarrow T_{NI}^G$; therefore, the rapid increase in τ near T_{NI}^G is not attributable to a change in G_s because an increase in modulus accelerates the shape recovery as shown in Figs. 3 and 4. This is further recognizable by the fact that τ at 25 °C is the smallest in the whole T range examined despite the highest degree of swelling ($Q \approx 15$), i.e., the lowest modulus [23]. The T dependence of τ is primarily ascribed to a change in local nematic order rather than network modulus and concentration. Nematic order parameter in general nematics decreases when $T \rightarrow T_{NI}$, and in particular, it steeply decreases in the vicinity of T_{NI} [24]. The marked change in τ near T_{NI}^G also indicates that the slow shape recovery mainly stems from the reorientation process of the constituent liquid crystals, not from other relaxation mechanisms (such as chain-entanglement relaxation). In contrast, the T dependence of γ_0 is due to a change in G_s (mainly resulting from that in Q). The considerably large γ_0 at 25 °C primarily results from the remarkably high Q . The T dependence of dry modulus (G_d) of polydomain LCEs near T_{NI} is an interesting issue [14]. The T dependence

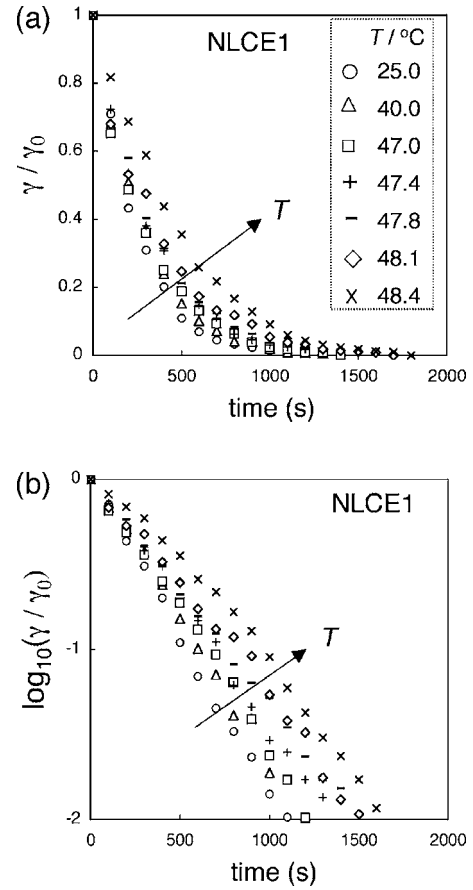


FIG. 6. (a) Time dependence of γ during the shape recovery of NLCE1 at various temperatures. The strain $\gamma(t)$ is reduced by the initial strain at each temperature. (b) Semilog plots of γ/γ_0 vs time at various temperatures. Symbols are the same as (a)

of γ_0 for the swollen LCEs includes the information about the T dependence of G_d , but it is also affected by Q . This complexity precludes the detailed discussion about the T dependence of G_d on the basis of that of γ_0 .

Figure 8 displays the double logarithmic plots of τ vs $(T_{NI}^G - T)$ for ILCE1 and NLCE1. The data points near T_{NI}^G trace a straight line with a slope of -0.22 or -0.16 for ILCE1 or NLCE1, respectively. The slopes were determined by the least square method. This suggests that the T dependence of τ near T_{NI}^G is expressed by the following power law [25]:

$$\tau \sim (T_{NI}^G - T)^{-x}, \quad (3)$$

where $x=0.22$ or 0.16 for ILCE1 and NLCE1, respectively. Two data points at the low temperatures do not obey this power law because the temperatures are far from T_{NI}^G . The similar values of x for ILCE1 and NLCE1 suggest that τ of these networks significantly differs in magnitude but their T dependences are similar. As Q near T_{NI}^G is weakly T dependent, the T dependence of τ involves the effect of network modulus. One may exclude this effect by reducing $\tau(T)$ by $Q(T)^{1/3}$, simply assuming $\tau \sim 1/G_s$ and $G_s \sim Q^{-1/3}$. The exponents x for the reduced τ of ILCE1 and NLCE1 are 0.24 and 0.18 , respectively, none of which are significantly altered from the x values for the original τ .

TABLE II. Degrees of equilibrium swelling and field-induced strain at various temperatures.

T (°C)	ILCE1		T (°C)	NLCE1	
	Q	$ \gamma_0 \times 10^2$		Q	$ \gamma_0 \times 10^2$
25.0	14.8	21.4	25.0	14.6	21.7
40.0	4.0	8.29	40.0	4.3	9.79
47.0	3.3	5.13	47.0	3.5	6.15
47.3	3.1	4.80	47.4	3.3	5.52
47.6	2.9	4.35	47.8	3.1	5.30
47.8	2.9	4.17	48.1	3.0	5.09
48.0	2.7	4.15	48.4	3.0	4.85

The time τ is determined by a balance between the restoring elastic force and the resisting viscous force. In general nematics, the Frank constants and viscous coefficients decrease when $T \rightarrow T_{\text{NI}}$ as a result of a reduction in local nematic order parameter (S) [24]. The present experimental results imply that the magnitude of the induced decrease in the elastic restoring force is larger than that of the viscous resistant force in polydomain LCEs. A related important phenomenon is the evolution of the domain size of polydomain LCEs near T_{NI} [18]. The domain size (ξ) steeply increases near T_{NI} as $\xi \sim (T_{\text{NI}} - T)^{-\gamma}$ with $\gamma = 1$. The domain size is determined by a balance between the Frank elasticity and the random disordering effect [3]. They estimated from the T

dependence of ξ that a coupling constant characterizing the random disordering effect (g) depends more strongly on S ($g \sim S^{3.5}$) than the Frank constant ($K \sim S^2$). The exponent x regarding τ is expected to correlate with the exponent γ regarding ξ , but the corresponding theory for polydomain LCE systems has not been established. The T dependence of S in polydomain LCE systems is important for the detailed discussion, but it has not yet been obtained because of the experimental difficulties to determine the order parameter regarding the individual local domain. Further theoretical and experimental efforts are needed for a complete understanding of the behavior of polydomain LCEs near T_{NI} .

IV. CONCLUSIONS

Polydomain LCEs composed of disordered nematic directors exhibit a slow shape recovery after the removal of the imposed field. The director alignment distribution at the cross-linking stage greatly influences the shape recovery dynamics in the resultant LCE, although it has no appreciable effect on the equilibrium and static properties such as the transition temperature, degree of swelling, and field-induced strain. The LCE formed in the polydomain nematic state shows a considerably faster shape recovery than that originally prepared in the isotropic state owing to the memory

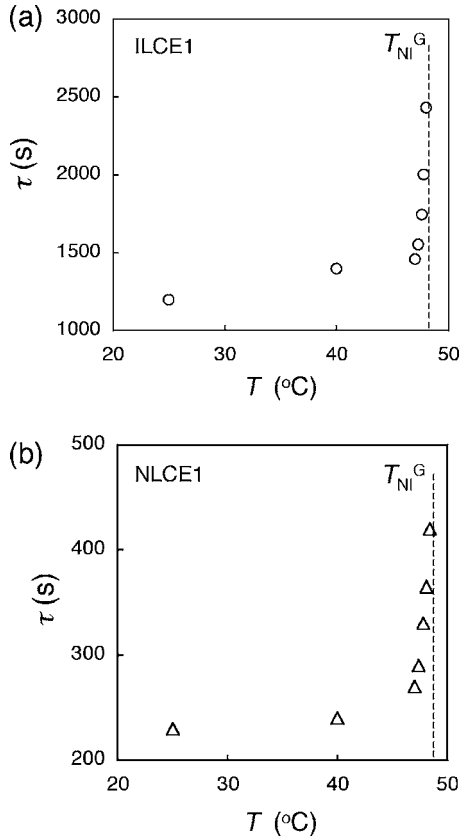


FIG. 7. Temperature (T) dependence of the longest relaxation time (τ) of (a) ILCE1 and (b) NLCE1. The N-I transition temperatures T_{NI}^{G} of ILCE1 and NLCE1 are 48.1 and 48.8 °C, respectively.

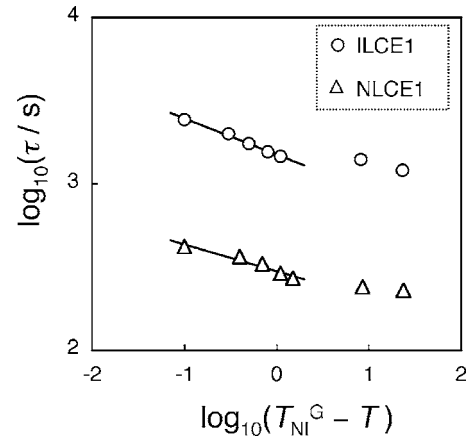


FIG. 8. Double-logarithmic plots of the longest relaxation time (τ) vs $(T_{\text{NI}}^{\text{G}} - T)$ where T_{NI}^{G} is the N-I transition temperature of the swollen LCE. The slope of the straight line is -0.22 and -0.16 for ILCE1 and NLCE1, respectively.

effect of the director distribution at the cross-linking stage. An increase in cross-linker concentration accelerates the shape recovery because of an increase in restoring force of rubber elasticity. The shape recovery process is described by an exponential-type relaxation function. The relaxation time steeply increases near the nematic-isotropic transition temperature, and the exponents in the power law for the relaxation time are estimated to be ~ 0.2 , which is independent of the initial director alignment at the cross-linking stage.

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